Claims:

1 A method of polymerising ethylenically unsaturated monomers in which at least one ethylenically unsaturated monomer is polymerised using a catalyst system having a manganese carbonyl radical initiator, a halogen containing reactive substrate and an allylic halogen substituted chain termination agent.

2 A method as claimed in claim 1 wherein the initiator is or includes a compound of the formula (I):

$$R^1\text{- Mn (CO)}_n\text{ (Lig)}_p \qquad (I)$$

where

R^1 is C_1 to C_{30} hydrocarbyl, or hydrocarbyl substituted with halogen, alkyl, alkoxy, acyl; or

R^1 is a group of the formula: - Mn $(CO)_n$ $(Lig)_p$ where Lig, n and p are as defined below;

each Lig is a ligand species;

n is from 1 to 5; and

p is from 0 to 4;

such that n + p = 5.

3 A method as claimed in claim 2 wherein the initiator is or includes a compound of the formula (Ia):

$$(Lig)_p\ (CO)_n\ Mn\text{- }Mn\ (CO)_n\ (Lig)_p \qquad (Ia)$$

where Lig, p and n are as defined for formula (I), such that p + n = 5.

4 A method as claimed in claim 3 wherein the initiator is dimanganese decacarbonyl.

5 A method as claimed in any one of claims 1 to 4 wherein the an allylic halogen substituted chain termination agent is a compound of the formula (II):

$$Hal\text{-}CHR^3\text{-}CR^4\text{=}CH2 \qquad (II)$$

where

Hal is halogen; and

R^3 and R^4 are each independently hydrogen, or a group: $(Link)_n$-R^5,

where:

n is 0 or 1,

Link is a linking group; and

R^5 is halogen, glycidyl, an ethylenic double bond, carbonyl, carboxyl, cyano, hydroxyl, amino or quaternary amino or ammonium, a phosphorus containing species, a sulphur containing species, a hydrogen bond donor or acceptor, an aromatic ring, a heterocyclic ring, or a saccharide residue.

6 A method as claimed in claim 5 wherein Hal is a chlorine or bromine atom.

7 A method as claimed in any one of claims 1 to 6 wherein the reactive substrate is also a chain terminating agent.

8 A method as claimed in any one of claims 1 to 6 wherein the reactive substrate is or includes a halogen substituted alkane, alcohol or carboxylic acid ester, an aromatic substituted alkyl halide, a ring substituted benzyl halide, or a sulphonyl halide.

9 A method as claimed in claim 8 wherein the reactive substrate has multiple halogen substitution.

10 A method as claimed in claim 8 wherein the reactive substrate is or includes carbon tetrachloride, carbon tetrabromide, chlorotribromomethane, trichloromethane, tribromomethane, dichloromethane, dibromomethane, 1,1-dichloroethane, 1,1-dibromoethane, 1,1,1-trichloroethane, 1,1,1-tribromoethane, 2,2-dichloroethanol, 2,2-dibromoethanol, 2,2,2-trichloroethanol, 2,2,2-tribromoethanol, trichloroacetic acid, C_1 to C_6 alkyl esters of trichloroacetic acid, C_2 to C_6 alkyl 2-bromo-2-methyl propionates, benzyl halides, 2-halo-2-phenylethanes, 4-alkyl benzyl halides, 4-fluorobenzyl bromide, 4-chlorobenzyl bromide, 4-fluorobenzyl chloride, 4-chlorobenzyl chloride, 1,2-di(bromomethyl)benzene, benzene sulphonyl chloride and toluene sulphonyl chloride.

11 A method as claimed in any one of claims 1 to 10 wherein the monomer is or includes one or more of an acrylic monomer, vinyl acetate, vinyl halide, styrene, α-methyl styrene, vinyl toluene, vinyl caprolactone, vinyl caprolactam or *N*-vinyl pyrollidone.

12 A method as claimed in claim 11 wherein the monomer includes at least 40 mole% of acrylic monomer or monomers.

13 A method as claimed in either claim 11 or claim 12 wherein the acrylic monomer is or includes monomer of the formula (IV):

$$R^{10}\text{-}CR^{11}=CR^{12}\text{-}COR^{13} \qquad \text{(IV)}$$

where

R^{10} is methyl or, and desirably, hydrogen;

R^{11} is methyl or, and desirably, hydrogen;

R^{12} is methyl or hydrogen;

provided that at least one of R^{11} and R^{12} is hydrogen, and

R^{13} is $-OR^{14}$, or $-NR^{15}R^{16}$ where R^{14}, R^{15} and R^{16} are each hydrogen, hydrocarbyl, or a polyalkyleneoxy chain.

14 A method as claimed in claim 13 wherein the monomer is or includes one or more acrylate or methacrylate ester; acrylic or methacrylic acid; acrylic or methacrylic amide; or a sulphonated acrylic monomer.

15 A method as claimed in any one of claims 1 to 14 wherein the reaction conditions include heating the reaction mixture containing the manganese carbonyl radical initiator to initiate thermolysis of the initiator.

16 A method as claimed in claim 15 wherein the reaction is carried out at a temperature of from 50 to 150°C, particularly 50 to 100°C.

17 A method as claimed in any one of claims 1 to 16 wherein the reaction conditions include exposing the reaction mixture containing the manganese carbonyl radical initiator to actinic radiation to initiate photolysis of the initiator.

18 A method as claimed in claim 17 wherein the actinic radiation is visible or ultraviolet light.

19 A method as claimed in either claim 17 or claim 18 wherein the reaction is carried out at a temperature of from -50 to 100°C.

20 A method as claimed in any one of claims 1 to 16 wherein the reaction mixture additionally includes a Lewis acid, particularly a metal containing Lewis acid.

21 A method as claimed in claim 20 wherein the Lewis acid is a magnesium salt, particularly a magnesium halide, such as magnesium bromide or magnesium chloride, a zinc salt, particularly a zinc halide, such as zinc bromide or zinc chloride, or zinc trifluoromethanesulfonate, a lanthanum salt such as lanthanum acetate, particularly as the heptahydrate, a ytterbium salt such as a ytterbium halide, particularly ytterbium chloride, or ytterbium triflate.

22 A catalyst system for polymerising ethylenically unsaturated monomers which is a combination of a manganese carbonyl radical initiator, a halogen containing reactive substrate and an allylic halogen substituted chain termination agent.

23 A catalyst system as claimed in claim 22 wherein the initiator is or includes a compound as defined in any one of claims 2 to 4.

24 A catalyst system as claimed in either claim 22 or claim 23 wherein the chain terminating agent is or includes a compound as defined in any one of claims 5 to 7.

25 A catalyst system as claimed in any one of claims 22 to 24 wherein the reactive substrate is also a chain terminating agent.

26 A catalyst system as claimed in any one of claims 22 to 24 wherein the reactive substrate is or includes a compound as defined in any one of claims 8 to 10.

27 A catalyst system as claimed in any one of claims 22 to 24 which additionally includes a Lewis acid, particularly a metal containing Lewis acid.

28 A catalyst system as claimed in claim 27 wherein the Lewis acid is a magnesium salt, particularly a magnesium halide, such as magnesium bromide or magnesium chloride, a zinc

salt, particularly a zinc halide, such as zinc bromide or zinc chloride, or zinc trifluoromethanesulfonate, a lanthanum salt such as lanthanum acetate, particularly as the heptahydrate, a ytterbium salt such as a ytterbium halide, particularly ytterbium chloride, or ytterbium triflate.

29 A polymer or copolymer of one or more ethylenically unsaturated monomers having at one end of the (co)polymeric chain a residue of a reactive substrate and a residue of a chain terminating agent at the other.

30 A polymer or copolymer as claimed in claim 29 wherein the (co)polymeric chain includes residues of one or more monomers as defined in any one of claims 11 to 14.

31 A polymer or copolymer as claimed in either claim 29 or claim 30 wherein the residue of the chain terminating agent is or includes the residue of a chain terminating agent as defined in any one of claims 5 to 7.

32 A polymer or copolymer as claimed in any one of claims 29 to 31 wherein the residue of the reactive substrate is or includes the residue of a reactive substrate as defined in any one of claims 8 to 10.